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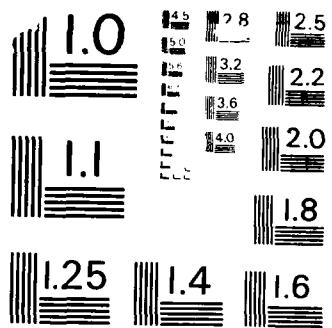
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Diode Laser Spectroscopy of Chemical Moieties at Surfaces

by

J.E. Butler, V.M. Bermudez, and R.L. Rubinovitz

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Diode Laser Spectroscopy of Chemical Moieties at Surfaces

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Abstract

The use of tunable infrared lead salt diode lasers as spectrally bright light sources for infrared reflection absorption spectroscopy (IRRAS) at interfaces will be presented. This new spectroscopy permits in-situ, non-intrusive optical probing of the vibrational fingerprint spectrum ($500\text{-}2000\text{ cm}^{-1}$) with sub-monolayer sensitivity at metal interfaces and can work through any moderately transmissive ambient. Recent results and instrumental developments will be presented.

Introduction

The nature of chemical species at a surface/interface plays an important role in the mechanisms of growth, removal of material, chemical transformation, and transport phenomena through the interface. These processes directly impact the growth of micro-electronic devices through epitaxial mechanisms (MBE, OMVPE), etching, deposition of interconnects, or protective coatings. Additional fields where the identification and understanding of these interfacial phenomena plays a critical role include catalysis, electrochemical cells, tribology, and corrosion, to name a few. Numerous spectroscopic techniques involving the scattering of energetic particles, ions, photons, or electrons have been developed by surface scientists for studying this inherently two dimensional environment.¹ Ideally, these techniques would have both selectivity to the surface environment and the sensitivity to detect the extremely small number of species ($\sim 10^{11}\text{-}10^{14}$ molecules/cm 2) which might represent a fraction of a monolayer coverage on the surface. Usually, compromises are made between the use of various complementary techniques to attain a sufficient understanding of the problem.

Various forms of vibrational spectroscopy have proven to be of great utility because of the "chemical fingerprint" nature of the vibrational spectrum of a molecule. The nature of chemical subgroups, degree of bonding, and symmetry of the environment are all distinguishable in the vibrational spectrum. This spectrum is usually accessed by the inelastic scattering of energetic photons (Raman scattering) or electrons (EELS), or the direct absorption or emission of an infrared photon. The use of energetic photons or electrons is often intrusive, e.g. can alter the environment which one is trying to probe. The EELS (electron energy loss spectroscopy) technique has been demonstrated to have high sensitivity and as a result is an extremely useful tool.² The major disadvantages with EELS are the necessity of a high vacuum environment and the possible chemical changes due to the energetic electrons.

IR reflection absorption spectroscopy (IRRAS) has been used to detect the vibrational spectrum of the surface chemical moieties.³ The principle advantages of this form of spectroscopy are: nearly every molecule possesses ir active modes, the low quantum energy of the photon (hence little perturbation of the environment), higher resolution over electron spectroscopies, and the ability to work in any moderately ir transmissive ambient, e.g. while chemical processing of the interface is occurring. The principle disadvantage lies in the sensitivity of the technique, which degrades for the longer wavelength/lower frequency modes due to the exponential fall-off of the spectral brightness of thermal ir radiation sources. Sensitivity as good as 0.001 monolayer has been achieved with a strong adsorber, CO, on metallic surfaces in the mid ir, 5-6 microns.³ However, in the important 10-30 micron region ($1000\text{-}330\text{ cm}^{-1}$), where many of the important metal-oxide/halide modes are, thermal sources have been inadequate.

In this work we shall describe our recent efforts to use tunable lead salt diode lasers as high brightness light sources for IRRAS studies. In the following we review the principles behind an IRRAS experiment, describe our experimental arrangement, and discuss the recent results on metallic and semiconductor/gas interferences.

Technique

In order to distinguish the extremely weak absorption of the ir radiation due to the molecules at the interface from absorptions in the optical path, it is useful to exploit

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the boundary conditions on the electromagnetic radiation at the interface. The simplest case to consider is that of the gas/metal interface where all tangential components of the electric field are zero in the plane of the interface for an ideal metal, i.e. the only non-zero component is perpendicular to the interface.⁴ There are two important implications of this boundary condition. First, that the molecules at the metal interface can be dipole excited only by those transitions which have a component of the transition moment perpendicular to the interface. And second, that the molecules at the interface will absorb radiation from only the portion of the light beam which is polarized in the plane of incidence (the plane formed by the normal to the interface and the propagation directions of the incident and reflected light waves), i.e. the "p" polarized component. The magnitude of the radiation polarized perpendicular to the plane of incidence, the "s" component, is zero at the surface and cannot couple to the molecules. The coupling of the "p" polarized wave to absorptions on the surface is maximum at grazing incidence where both the projection of the electric field on the surface normal and the number of surface molecules probed per unit fluence combine to give sensitivities as much as 100 times greater than for similar gas phase absorptions.⁴ This "lowered" symmetry at the interface can also be exploited for non-metallic interfaces, but with significantly less surface enhancement.^{5,6}

In these experiments we employ two types of polarization modulation techniques to measure the differential absorption between the "s" (reference) and "p" (signal) polarized components. These have the advantages of detecting the weak absorptions on a small differential signal rather than on a large background and of discriminating against any homogeneous absorptions in the optical path (gases, windows, etc.). Two methods are employed for polarization modulation. In the first method, the interface to be studied is placed between two polarizers, one fixed at an angle relative to the plane of incidence which gives equal intensity in both the "p" and "s" polarized reflected waves, and the other rotating so that it alternately samples each polarization component.⁷ In the second method, both polarizers remain fixed and a photoelastic modulator is inserted along with the interface in the optical path between the two polarizers.⁸ This photoelastic modulator introduces a oscillating phase delay between the two polarization components,⁹ which for a suitably chosen amplitude, gives a signal at the second harmonic of the oscillation frequency that is proportional to the difference between reflected intensities of the two polarization components. These two techniques are described in detail in references 5,7, and 9.

Lead salt tunable diode lasers¹⁰ are light sources which emit infrared radiation ($300\text{-}3600\text{ cm}^{-1}$) at modest power levels (0.1-10 mw) with an extremely narrow bandwidth (5MHz) in a narrow distribution of longitudinal modes ($20\text{-}30\text{ cm}^{-1}$) spaced by $2\text{-}3\text{ cm}^{-1}$. The wavenumber of the group of longitudinal modes can be tuned over a range as large as $200\text{-}800\text{ cm}^{-1}$ by the temperature dependence of the bandgap of the diode. High resolution tuning of the individual modes is achieved by finely adjusting the length and the refractive index of the crystal by slight variations of the current or temperature of the diode. These light sources have traditionally been employed in applications which require high resolution for determining molecular structures or in detecting trace components. Since high resolution features are not expected in most interfacial environments, these experiments will exploit the high spectral brightness of the diode lasers ($\sim 10^4 \times$ black body sources) and coarse tunability via the temperature dependence of the bandgap to examine IRRAS features at lower wavenumbers than can be probed currently by conventional black body source IRRAS spectrometers.

We have used three methods of tuning the diode laser for scanning an IRRAS spectrum. In the first method the full power spectrum of the laser, operating well above threshold, was tuned continuously by heating the diode up to near its maximum operating temperature and then shutting off the heater and letting the refrigerator cool the diode at its natural rate. This resulted in "low" resolution scans, where the envelope of the laser modes was $20\text{-}30\text{ cm}^{-1}$, covering $200\text{-}250\text{ cm}^{-1}$. In the second method, the diode laser temperature was scanned in steps using the full power spectrum. This resulted in spectra similar to those obtained by the first method, but with a slight improvement in sensitivity. In the third method, the resolution was increased by using a monochromator to select the individual modes of the diode laser at each temperature step. The resolution was increased to ca. 3 cm^{-1} , but at an expense of longer scan times and higher noise levels.

Results

We have observed the initial stages of oxidation of polycrystalline Al by O₂ using the continuous temperature scan method and modulating the polarization by a rotating polarizer.⁷ Partially resolved bands attributed to surface site Al-O stretches were observed at 560 and 640 cm^{-1} ,^{11,12} A broad, structured band attributed to sub-surface Al-O stretches^{11,12} was also observed between $820\text{-}1000\text{ cm}^{-1}$. These initial experiments had a noise level of ca. 0.2% and demonstrated the utility of the diode laser for probing sub-monolayer concentrations at metallic interfaces.

Our recent experiments have focussed on achieving the sensitivity to detect sub-monolayer concentrations at semiconductor interfaces. Polarization modulation in these experiments was achieved using a ZnSe photoelastic modulator at 31 KHz. Scans which employed the monochromator to select individual laser modes had a noise level of ca. 0.1% which was insufficient sensitivity for observing monolayers of fluorine or oxygen species on Si. When the full power spectrum of the diode was used with the temperature step scans, noise levels of 0.005% to 0.02% were obtained. This has enabled the recent observation of oxide growth on single crystals of Si(111) which had been cleaned in a dilute solution of HF and then etched by F atoms entrained in He at 1 torr before exposure to air. The initial exposure gave rise to a band at 720 cm⁻¹. Extended exposure to air increased the absorption at 720 and gave rise to a new and stronger band at 800 cm⁻¹. The range scanned in these experiments was 650 to 850 cm⁻¹.

Conclusions

Tunable lead salt laser diodes have been shown to be useful light sources for obtaining the vibrational spectra of chemical species at interfaces. The three principal advantages of this surface spectroscopy over other methods of probing the surface are 1) it is non-intrusive, 2) it does not require a high vacuum environment, and 3) it extends the useful range of ir spectroscopy on surfaces to the important 350-1200 cm⁻¹ region.

Acknowledgements

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